Electronic Supplementary Information for

Platinum(II) photo-catalysis for highly selective difluoroalkylation

reactions

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1. Experimental section

a) General information

All chemicals, unless otherwise noted, were purchased from commercial sources and were used without further purification. All solvents for photophysical studies were of HPLC grade. Unless stated otherwise, all reactions were carried out under nitrogen. The ligands of the Pt(II) complexes were synthesized according to literature methods.¹⁻⁴ Irradiation with visible light was performed using blue LEDs illumination instruments.

The nuclear magnetic resonance spectra were recorded on the Bruker AscendTM 400 MHz NMR spectrometer and the Bruker AscendTM 500 MHz NMR spectrometer with tetramethylsilane (TMS) as an internal standard. High resolution mass spectra were recorded using a Q Exactive mass spectrometer (Thermo Fisher Scientific, USA). The absorption spectra were recorded on a Thermo Scientific Evolution 201 UV/Visible Spectrophotometer. The emission spectra were recorded on an Edinburg spectrometer FLS-980 equipped with MCP-PMT detectors. X-Ray diffraction data of the single crystal were collected on Bruker X8 Proteum diffractometer.

b) Method for the synthesis of the Pt(II) complexes 1, 3, 5 and 6



Scheme S1. Synthesis of the Pt(II) complexes 1, 3, 5 and 6.

The Pt(II) complexes were easily synthesized by the combination of the precursors $Pt^{II}(C^N^N)Cl$ and diphosphine ligands as shown in Scheme S1. The precursors $Pt^{II}(C^N^N)Cl$ were synthesized according to the previous reported literatures.¹ A mixture of $Pt^{II}(C^N^N)Cl$ and equimolar diphosphine ligand in CH₃CN:CH₃OH (1:1 v/v) was stirred for about 4 h until all the substrates were dissolved in the solution

under nitrogen atmosphere. The reaction mixture was evaporated and purified with neutral alumina column chromatography using $CH_2Cl_2:CH_3OH$ (100:1) as eluent. Nearly quantitative amount of the desired Pt(II) complexes $Pt^{II}(C^N)(P^P)Cl$ could be obtained. Addition of methanol solution of NH_4BF_4 into methanol solution of $Pt^{II}(C^N)(P^P)Cl$ resulted in the generation of $[Pt^{II}(C^N)(P^P)]BF_4$.

Pt(II) complex 1: ¹**H NMR** (500 MHz, CD₃OD) $\delta = 8.70$ (s, 2H), 8.40 (s, 1H), 8.12 (d, J = 7.7 Hz, 1H), 7.87 – 7.71 (m, 8H), 7.69 – 7.42 (m, 6H), 7.41 – 7.09 (m, 14H), 6.97 (t, J = 7.6 Hz, 1H), 6.84 (t, J = 7.6 Hz, 1H), 6.71 (t, J = 7.3 Hz, 1H), 6.56 (m, 5H), 6.45 (t, J = 6.9 Hz, 2H), 6.38 (d, J = 8.7 Hz, 1H), 6.26 – 6.17 (m, 2H), 6.10 (d, J = 8.6 Hz, 1H), 3.94 (s, 3H). ³¹**P NMR** (202 MHz, CD₃OD) $\delta = 14.05$ (d, J = 24.2 Hz), 13.35 (d, J = 24.1 Hz). **HRMS** (ESI) (m/z): [M]⁺ calcd. for C₆₇H₄₉ON₂P₂Pt: 1154.2962, found: 1154.2960.

Pt(II) complex 3: ¹**H NMR** (400 MHz, CD₃OD) $\delta = 8.75$ (s, 3H), 8.18 (d, J = 8.2 Hz, 1H), 8.04 – 7.85 (m, 3H), 7.84 – 7.68 (m, 5H), 7.60 (dt, J = 17.5, 9.0 Hz, 5H), 7.46 (s, 2H), 7.40 – 7.27 (m, 6H), 7.24 – 7.11 (m, 3H), 6.96 (s, 2H), 6.84 (t, J = 9.5 Hz, 1H), 6.71 (m, 1H), 6.66 – 6.50 (m, 5H), 6.44 (m, 2H), 6.37 (d, J = 8.7 Hz, 1H), 6.21 (m, 2H), 6.10 (d, J = 8.5 Hz, 1H). ³¹**P NMR** (162 MHz, CD₃OD) $\delta = 14.19$ (d, J = 24.3 Hz), 13.17 (d, J = 24.3 Hz). **HRMS** (ESI) (m/z): [M]⁺ calcd. for C₆₀H₄₃N₂P₂Pt: 1048.2544, found: 1048.2534.

Pt(II) complex 5: ¹**H NMR** (500 MHz, CD₃OD) δ = 8.76 (s, 2H), 8.38 (s, 1H), 8.13 (d, *J* = 7.6 Hz, 1H), 7.91 – 7.74 (m, 7H), 7.63 – 7.51 (m, 1H), 7.39 – 7.08 (m, 18H), 6.97 – 6.88 (m, 6H), 6.68 – 6.63 (m, 2H), 6.28 – 6.22 (m, 3H), 6.03 (s, 1H), 3.93 (s, 3H). ³¹**P NMR** (202 MHz, DMSO) δ = 12.20 (s), 10.80 (s), -144.21 (hept, *J* = 706.0 Hz). **HRMS** (ESI) (m/z): [M]⁺ calcd. for C₅₉H₄₅ON₂P₂Pt: 1054.2649, found: 1054.2629.

Pt(II) complex 6: ¹**H NMR** (500 MHz, CD₃CN) δ = 8.24 (d, *J* = 4.2 Hz, 1H), 8.08 (s, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.83 – 7.75 (m, 3H), 7.70 (s, 1H), 7.64 – 7.21 (m, 25H), 7.17 – 7.03 (m, 4H), 6.85 (dd, *J* = 7.2, 4.9 Hz, 1H), 6.67 (t, *J* = 7.3 Hz, 1H), 3.90 (s, 3H). ³¹**P NMR** (202 MHz, CD₃CN) δ = 44.56 (s), 37.50 (s), -144.63 (hept, *J* = 706.3 Hz). **HRMS** (ESI) (m/z): [M]⁺ calcd. for C₅₃H₄₁ON₂P₂Pt: 978.2336, found: 978.2328.



c) Method for the synthesis of the Pt(II) complexes 2 and 4

Scheme S2. Synthesis of the Pt(II) complex 2.

The synthesis of Pt(II) complex 2 was illustrated in Scheme S2 reference to the literatures.²⁻⁴ Details for the synthesis are shown as following:

(1). Acetophenone (2.64 g, 22.0 mmol) and pyridine (5.0 mL, 61.8 mmol) were dissolved in 10 mL ethanol. Then NH₂OH•HCl (2.29 g, 33.0 mmol) was added. The reaction mixture was stirred at 60 °C for 1 h. The reaction was quenched by water and the organic layer was extracted with ethyl acetate. The combined organic phases were washed with 1 N aqueous HCl and brine, and dried over NaSO₄. The solvent was removed by rotary evaporation to give the crude product acetophenone oxime.

(2). The crude product acetophenone oxime dissolved in 10 mL pyridine was treated with Ac_2O (4.2 mL, 44.4 mmol) and a catalytic amount of DMAP (5 mg). The mixture was stirred at room temperature for 1 h. The reaction was treated with water and was extracted with ethyl acetate. The combined organic phases were washed with

1 N aqueous HCl and brine, and dried over NaSO₄. The solvent was removed by rotary evaporation to give the crude product acetophenone O-acetyl oxime. Further recrystallization from ethyl acetate-hexane was conducted to provide *E*-acetophenone O-acetyl oxime.

(3). A 50 mL round-bottom flask equipped with a stirrer bar was charged with *E*-acetophenone *O*-acetyl oxime (5 mmol, 885 mg) and CuI (190 mg, 1 mmol, 20 mol%). The round-bottom flask was quickly evacuated and refilled with N₂ for three times, followed by the addition of α , β -unsaturated aldehyde (8 mmol, 1.3 g), diisopropylamine (10 mmol, 1.01 g), and DMSO (20 mL). Then the reaction mixture was stirred at 60 °C for 16 h. Upon cooling to room temperature, the reaction mixture was washed with water and extracted with ethyl acetate. The combined organic phase was dried over Na₂SO₄. The solvent was removed by rotary evaporation. The residue was purified by flash chromatography on silica gel to afford the C^N ligand.

(4). An aqueous degassed solution (5 mL) of potassium tetrachloroplatinate (415 mg, 1.0 mmol) was added under N_2 to a stirred degassed solution of the above C^N ligand (261 mg, 1.0 mmol) in 15 mL 2-ethoxyethanol. The reaction mixture was heated to 80 °C for 24 h. After cooling in an ice bath, distilled water was added. The precipitate was filtered, washed with ethanol and dried under vacuum.

(5). A mixture of the precipitate in (4) and 2.0 equivalents of *R*-BINAP was dissolved in CH₂Cl₂:DMSO (1:1 v/v), the mixture was stirred for about 4 h until all the substrates were dissolved in the solution under nitrogen atmosphere. The reaction mixture was washed with water and extracted with dichloromethane. The dichloromethane was dried over Na₂SO₄. The solvent was removed by rotary evaporation to give the desired Pt(II) complex **2** quantitatively.

Pt(II) complex **2**: ¹**H NMR** (400 MHz, DMSO) $\delta = 8.41$ (s, 1H), 8.13 (d, J = 7.9 Hz, 1H), 7.92 (d, J = 8.9 Hz, 2H), 7.85 – 7.66 (m, 7H), 7.63 – 7.54 (m, 3H), 7.54 – 7.42 (m, 8H), 7.40 – 7.30 (m, 2H), 7.25 – 7.21 (m, 2H), 7.19 – 7.12 (m, 4H), 7.11 – 7.00 (m, 5H), 6.98 – 6.89 (m, 2H), 6.71 (d, J = 8.6 Hz, 1H), 6.66 – 6.53 (m, 3H), 6.52 – 6.44 (m, 2H), 3.84 (s, 3H). ³¹P NMR (162 MHz, DMSO) $\delta = 21.90$ (d, J = 22.7 Hz), 16.42 (d, J = 22.7 Hz). **HRMS** (ESI) (m/z): [M]⁺ calcd. for C₆₂H₄₆ONP₂Pt: 1077.2697, found: 1077.2709.



Scheme S3. Synthesis of the Pt(II) complex 4.

The synthesis of Pt(II) complex **4** was illustrated in Scheme S3. Details for the synthesis are shown as following:

(6). An aqueous degassed solution (5 mL) of potassium tetrachloroplatinate (415 mg, 1.0 mmol) was added under N₂ to a stirred degassed solution of the 2-phenylpyridine (155 mg, 1.0 mmol) in 15 mL 2-ethoxyethanol. The reaction mixture was heated to 80 % for 24 h. After cooling in an ice bath, distilled water was added. The precipitate was filtered, washed with ethanol and dried under vacuum.

(7). A mixture of the precipitate in (6) and 2.0 equivalents of *R*-BINAP was dissolved in CH₂Cl₂:DMSO (1:1 v/v), the mixture was stirred for about 4 h until all the substrates were dissolved in the solution under nitrogen atmosphere. The reaction mixture was washed with water and extracted with dichloromethane. The dichloromethane was dried over Na₂SO₄. The solvent was removed by rotary evaporation to give the desired Pt(II) complex **4** quantitatively.

Pt(II) complex **4**: ¹H NMR (400 MHz, DMSO) $\delta = 8.58$ (s, 2H), 8.17 (d, J = 8.2 Hz, 1H), 7.95 (t, J = 7.8 Hz, 1H), 7.91 – 7.62 (m, 9H), 7.61 – 7.30 (m, 10H), 7.27 – 7.08 (m, 5H), 7.08 – 6.78 (m, 6H), 6.77 – 6.28 (m, 6H). ³¹P NMR (162 MHz, DMSO) $\delta = 22.16$ (d, J = 22.6 Hz), 16.19 (d, J = 22.7 Hz). **HRMS** (ESI) (m/z): [M]⁺ calcd. for C₅₅H₄₀NP₂Pt: 971.2278, found: 971.2273.

d) Crystal structure determination of 1

Single crystals of **1** were prepared by dispersing hexane into minimal amount of methanol solution of **1**. The X-ray diffraction data were collected on a Bruker X8 Proteum diffractometer equipped with a **'Bruker APEX-II CCD'** detector. The crystal was kept at 100 K during data collection. The diffraction images were interpreted and the diffraction intensities were integrated by using the program SAINT. Multi-scan SADABS was applied for absorption correction. By using Olex2,⁵ the structure was solved with the XS⁶ structure solution program using direct Methods and refined with the XL⁶ refinement package using Least Squares minimization. The positions of the H atoms were calculated on the basis of the riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, 1.5 times that of the C atoms in methyl group and these positions participated in the calculation of the final R indices. In the final stage of least-squares refinement, all non-hydrogen atoms were refined anisotropically.

Identification code 1	
Empirical formula	$C_{135}H_{102}B_2F_8N_4O_3P_4Pt_2$
Formula weight	2515.88
Temperature/K	100
Crystal system	Triclinic
Space group	P1
a/Å	11.2381(7)
b/Å	14.8266(9)
c/Å	16.8813(10)
α/°	97.7440(10)
β/°	98.3340(10)
γ/°	101.0580(10)
Volume/Å ³	2692.9(3)
Z	1
$\rho_{calc}g/cm^3$	1.551
μ/mm^{-1}	5.949
F(000)	1262
Crystal size/mm ³	$0.26 \times 0.25 \times 0.22$
Radiation	$CuK\alpha (\lambda = 1.54178)$
2Θ range for data collection/°	5.366 to 133.608
Index ranges	$-13 \leqslant h \leqslant 9, -17 \leqslant k \leqslant 17, -19 \leqslant l \leqslant 19$
Reflections collected	51084
Independent reflections	11133 [$R_{int} = 0.0453$, $R_{sigma} = 0.0416$]
Data/restraints/parameters	11133/3/1427
Goodness-of-fit on F ²	1.051
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0248, wR_2 = 0.0610$
Final R indexes [all data]	$R_1 = 0.0248, wR_2 = 0.0610$
Largest diff. peak/hole / e Å ⁻³	0.96/-0.70
Flack parameter	0.007(4)

 Table S1. Crystal data and structure refinement for 1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å	
Pt1	P1	2.2494(1)	Pt2	P3	2.3538(1)	
Pt1	P2	2.3506(1)	Pt2	P4	2.2460(1)	
Pt1	N1	2.113(4)	Pt2	N3	2.112(4)	
Pt1	C68	2.066(5)	Pt2	C1	2.068(5)	

 Table S2. Selected bond lengths for 1.

Table S3. Selected bond angles(°) for 1.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P1	Pt1	P2	92.95(4)	P4	Pt2	P3	91.73(4)
N1	Pt1	P1	169.79(1)	N3	Pt2	P3	96.01(1)
N1	Pt1	P2	94.94(1)	N3	Pt2	P4	170.66(1)
C68	Pt1	P1	96.32(1)	C1	Pt2	P3	154.49(1)
C68	Pt1	P2	157.18(1)	C1	Pt2	P4	96.38(1)
C68	Pt1	N1	78.73(2)	C1	Pt2	N3	78.78(2)

e) General procedure for visible-light-induced difluoroalkylation of cinnamic acids and terminal alkynes catalyzed by the Pt(II) complexes

The cinnamic acid derivatives (or terminal alkynes) (0.2 mmol, 1 equiv.), ethyldifluoroiodoacetate (0.22 mmol, 1.1 equiv.), sodium dicarbonate (0.22 mmol, 1.1 equiv.) (5.0 equiv. DIPEA) and the Pt(II) complex **1** (0.001 mmol, 0.5 mol%) were dissolved in 5.0 mL CH₃CN (CH₃CN:CH₃OH) in a 15 mL reaction tube equipped with magnetic stirring bar, the reaction tube was sealed and the resulting mixture was deaerated with nitrogen for 15 min, then the reaction tube was irradiated by blue LEDs for 12 h. After reaction, the organic layer was extracted with diethyl ether (3 × 5 mL). The combined organic phases were washed with brine and dried over sodium sulphate. The solvent was removed by rotary evaporation and purified by column chromatography on silica gel using hexane/ethyl acetate (25:1) as the eluent.



Fig. S1 Nano-second time-resolved emission (ns-TRE), absorption (ns-TA) spectra, kinetic decay trace of a) selected emission and b) absorption peaks, c), d) and their decay fitting plots of **1** (concentration ca. 1.0×10^{-5} M) in degassed acetonitrile at room temperature.



Fig. S2 Cyclic voltammogram of **1** $(1.0 \times 10^{-3} \text{ M})$ in degassed acetonitrile at 298 K (with 0.1 M ^{*n*}Bu₄NPF₆ as supporting electrolyte; Ag/AgNO₃ (0.1 M in CH₃CN) reference electrode; scanning rate: 50 mV s⁻¹; Cp₂Fe^{+/0} occurs at 0.1 V *vs* Ag/AgNO₃).



Fig. S3 HRMS spectra of 1 in the presence of substrate b1.



Fig. S4 ns-TA spectra of $1 (5 \times 10^{5} \text{ M})$ in CH₃CN in the presence of 20 equiv. of substrates **a1**, **a1+b1**, **b1**, **a1**, and **a1+b1** (1 mM for each component) after 355 nm laser excitation recorded at a) 0 s and b) 20 µs. The kinetic studies for absorption bleaches at c) 363 nm; d) 400 nm. e) is to show the growth process for absorption at 400 nm; f) UV/Vis absorption spectra and g) emission spectra of above solutions. h) is to show the reaction between **a1**⁻ and •R_F from time-resolved spectroscopic methods.

Details on purification/synthesis of substrates used in time-resolved spectroscopic measurements:

Substrate **b1** (ca. 5 mL; brown color) was further purified by treating with saturated $Na_2S_2O_3$ aqueous solution (5 mL), dried by MgSO₄, and passed through a short pad of celite, about 3 mL of **b1** was received before photo-physical examination. Substrate **a1**⁻ (with counter cation of NBu_4^+) was synthesized by combining the methanolic solution of **a1** (3 mmol in 3 mL) and NBu₄OH (1 M/L; 3 mL) and removing the methanol solvent to give a quantity yield.



Fig. S5 Cyclic voltammogram of **b1** (ICF₂CO₂Et; 1.0×10^{-3} M), **b2** (BrCF₂CO₂Et; 1.0×10^{-3} M) in degassed acetonitrile at 298 K (with 0.1 M ^{*n*}Bu₄NPF₆ as supporting electrolyte; Ag/AgNO₃ (0.1 M in CH₃CN) reference electrode; scanning rate: 50 mV s⁻¹).



Scheme S4. The terminal alkene styrene was conducted in the reaction.



Scheme S5. Plausible reaction pathway.

f) References

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2. Characterization data of the products



¹**H NMR** (400 MHz, CDCl₃) δ = 7.93 – 7.47 (m, 2H), 7.44 – 7.33 (m, 3H), 7.11 (dt, *J* = 16.2, 2.5 Hz, 1H), 6.34 (dt, *J* = 16.2, 11.4 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ = 163.95 (t, *J* = 35 Hz), 136.86 (t, *J* = 10 Hz), 134.13, 129.67, 128.86, 127.47, 118.87 (t, *J* = 25 Hz), 112.76 (t, *J* = 247.5 Hz), 63.14, 13.97. ¹⁹**F NMR** (376 MHz, CDCl₃) δ = -103.20 (dd, *J* = 11.4, 3.7 Hz, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{12}H_{13}F_2O_2$: 227.0878, found: 227.0874.



¹**H** NMR (400 MHz, CDCl₃) δ = 7.37 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.08 (dt, *J* = 16.2, 2.5 Hz, 1H), 6.29 (dt, *J* = 16.2, 11.5 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ = 164.04 (t, *J* = 35 Hz), 139.88, 136.76 (t, *J* = 10 Hz), 131.39, 129.56, 127.41, 117.78 (t, *J* = 25 Hz), 112.90 (t, *J* = 247 Hz), 63.06, 21.33, 13.96.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -102.93 (dd, *J* = 11.5, 2.4 Hz, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{13}H_{15}F_2O_2$: 241.1035, found: 241.1030.



¹**H NMR** (500 MHz, CDCl₃) δ = 7.48 (d, *J* = 8.6 Hz, 2H), 7.13 (d, *J* = 8.6 Hz, 2H), 7.08 (dt, *J* = 16.2, 2.3 Hz, 1H), 6.28 (dt, *J* = 16.2, 11.4 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.33 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ = 169.24, 163.86 (t, *J* = 35 Hz), 151.60, 135.81 (t, *J* = 9.4 Hz), 131.85, 128.57, 122.11, 119.06 (t, *J* = 25 Hz), 112.64 (t, *J* = 247.5 Hz), 63.19, 21.12, 13.97.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -103.29 (s, 2F).

HRMS (ESI) (m/z): $[M+Na]^+$ calcd. for $C_{14}H_{14}F_2O_4Na$: 307.0752, found: 307.0745.



¹**H** NMR (400 MHz, CDCl₃) δ = 10.05 (s, 1H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.16 (dt, *J* = 16.2 Hz, 2.5, 1H), 6.47 (dt, *J* = 16.2 Hz, 11.3, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ = 191.42, 163.55 (t, J = 34.5 Hz), 139.79, 136.87, 135.56 (t, J = 9.4 Hz), 130.16, 128.02, 122.15 (t, J = 25 Hz), 112.30 (t, J = 248 Hz), 63.33, 13.95.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -103.74 (s, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{13}H_{13}F_2O_3$: 255.0827, found: 255.0824.



¹**H NMR** (400 MHz, CDCl₃) δ = 7.41 (d, *J* = 8.7 Hz, 2H), 7.04 (dt, *J* = 16.2, 2.5 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.19 (dt, *J* = 16.2, 11.5 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ = 164.13 (t, J = 35 Hz), 160.80, 136.33 (t, J = 9.5 Hz), 128.94, 126.80, 116.34 (t, J = 24.5 Hz), 114.24, 113.01 (t, J = 247 Hz), 63.07, 55.35, 13.98.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -102.67 (s, 2F).

HRMS (ESI) (m/z): [M+Na]⁺ calcd. for C₁₃H₁₄F₂O₃Na: 279.0803, found: 279.0798.



¹**H NMR** (400 MHz, CDCl₃) δ = 7.50 (d, *J* = 7.8 Hz, 1H), 7.38 (dt, *J* = 16.1, 2.6 Hz, 1H), 7.30 – 7.19 (m, 3H), 6.25 (dt, *J* = 16.1, 11.4 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ = 163.99 (t, *J* = 34.9 Hz), 136.79, 134.70 (t, *J* = 9.4 Hz), 133.24, 130.68, 129.45, 126.37, 126.12, 120.09 (t, *J* = 24.5 Hz), 112.77 (t, *J* = 248.4 Hz), 63.13, 19.66, 13.99. ¹⁹F NMR (376 MHz, CDCl₃) δ = -103.06 (s, 2F).

HRMS (ESI) (m/z): $[M+Na]^+$ calcd. for $C_{13}H_{14}F_2O_2Na$: 263.0854, found: 263.0852.



¹**H** NMR (400 MHz, CDCl₃) δ = 7.33 – 7.28 (m, 1H), 7.11 – 7.04 (m, 2H), 7.01 – 6.98 (m, 1H), 6.93 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.32 (dt, *J* = 16.2, 11.4 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ = 163.92 (t, *J* = 35 Hz), 159.93, 136.79 (t, *J* = 9.4 Hz), 135.50, 129.88, 120.08, 119.16 (t, *J* = 25 Hz), 112.71(t, *J* = 247.5 Hz), 112.61, 63.15, 55.31, 13.96.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -103.23 (s, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{13}H_{15}F_2O_3$: 257.0984, found: 257.0978.



¹**H NMR** (400 MHz, CDCl₃) δ = 7.28 (t, *J* = 2.8 Hz, 3H), 7.22 – 7.18 (m, 1H), 7.07 (dt, *J* = 16.2, 2.5 Hz, 1H), 6.31 (dt, *J* = 16.2, 11.5 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ = 164.01 (t, J = 35.1 Hz), 138.54, 136.97 (t, J = 9.4 Hz), 134.06, 130.47, 128.75, 128.11, 124.66, 118.60 (t, J = 25.0 Hz), 112.80 (t, J = 248.5 Hz), 63.12, 21.34, 13.99. ¹⁹F NMR (376 MHz, CDCl₃) δ = -103.22 (s, 2F).

HRMS (ESI) (m/z): $[M+Na]^+$ calcd. for $C_{13}H_{14}F_2O_2Na$: 263.0854, found: 263.0853.



¹**H NMR** (400 MHz, CDCl₃) δ = 7.38 (d, *J* = 8.4 Hz), 7.24 (d, *J* = 8.4 Hz, 2H), 7.04 (dt, *J* = 16.2, 2.5 Hz, 1H), 6.27 (dt, *J* = 16.2, 11.4 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.51 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ = 163.96 (t, *J* = 34.9 Hz), 140.94, 136.21 (t, *J* = 9.5 Hz), 130.71,

127.81, 126.16, 117.89 (t, *J* = 25.0 Hz), 112.82 (t, *J* = 248.5 Hz), 63.12, 15.29, 13.97.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -102.96 (dd, *J* = 11.5, 2.5 Hz, 2F).

HRMS (ESI) (m/z): [M+Na]⁺ calcd. for C₁₃H₁₄SF₂O₂Na: 295.0575, found: 295.0576.



¹**H NMR** (500 MHz, CDCl₃) δ = 7.37 – 7.30 (m, 2H), 7.12 – 7.08 (m, 2H), 6.23 (dt, *J* = 16.1, 11.4 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 2.36 (d, *J* = 4.1 Hz, 6H), 1.40 (t, *J* = 7.1 Hz, 3H). ¹³**C NMR** (125 MHz, CDCl₃) δ = 164.05 (t, *J* = 35 Hz), 135.80, 134.71 (t, *J* = 9.4 Hz), 133.76, 132.96, 130.60, 130.26, 126.65, 119.73 (t, *J* = 25 Hz), 112.82 (t, *J* = 247.5 Hz), 63.11, 20.95, 19.17, 14.00. ¹⁹**F NMR** (376 MHz, CDCl₃) δ = -102.96 (s, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{14}H_{17}F_2O_2$: 255.1191, found: 255.1185.



¹**H NMR** (400 MHz, CDCl₃) δ = 7.39 (d, *J* = 8.5 Hz, 1H), 7.32 (dt, *J* = 16.1, 2.5 Hz, 1H), 7.04 (d, *J* = 7.0 Hz, 2H), 6.19 (dt, *J* = 16.1, 11.4 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 2.35 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ = 164.09 (t, J = 35.0 Hz), 139.56, 136.70, 134.49 (t, J = 9.4 Hz), 131.44, 130.35, 127.11, 126.02, 118.94 (t, J = 24.8 Hz), 112.89 (t, J = 248.2 Hz), 63.07, 21.22, 19.59, 14.00.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -102.87 (s, 2F).

HRMS (ESI) (m/z): $[M+Na]^+$ calcd. for $C_{14}H_{16}F_2O_2Na$: 277.1011, found: 277.1015.



¹**H NMR** (400 MHz, CDCl₃) δ = 7.00 (dt, *J* = 16.1, 2.4 Hz, 1H), 6.68 (s, 2H), 6.22 (dt, *J* = 16.1, 11.4 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.91 – 3.85 (m, 9H), 1.37 (t, *J* = 7.1 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ = 163.96 (t, *J* = 34.9 Hz), 153.47, 139.53, 136.83 (t, *J* = 9.5 Hz),

129.67, 118.16 (t, *J* = 25.0 Hz), 112.74 (t, *J* = 248.7 Hz), 104.67, 63.14, 60.92, 56.17, 13.94.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -102.96 (s, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{15}H_{19}F_2O_5$: 317.1195, found: 317.1187.



¹**H NMR** (400 MHz, CDCl₃) δ = 7.49 (td, *J* = 7.6, 1.5 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.23 (dt, *J* = 16.4, 2.6 Hz, 1H), 7.20 – 7.15 (m, 1H), 7.14 – 7.09 (m, 1H), 6.46 (dt, *J* = 16.4, 11.3 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ = 163.80 (t, *J* = 35 Hz), 160.95 (d, *J* = 251 Hz), 131.14 (d, *J* = 8.7 Hz), 129.78 (td, *J* = 11.5, 8.4, 3.2 Hz), 128.63 (d, *J* = 2.9 Hz), 124.42 (d, *J* = 3.7 Hz), 122.06 (d, *J* = 11.5 Hz), 121.46 (td, *J* = 25.0, 7.1 Hz), 116.13 (d, *J* = 20 Hz), 112.57 (t, *J* = 248 Hz), 63.20, 13.95. ¹⁹F NMR (376 MHz, CDCl₃) δ = -103.70 (s, 2F), -115.68 (s, 1F).

HRMS (ESI) (m/z): $[M+Na]^+$ calcd. for $C_{12}H_{11}F_3O_2Na$: 267.0603, found: 267.0602.



¹**H NMR** (400 MHz, CDCl₃) δ = 7.51 – 7.40 (m, 2H), 7.14 – 7.01 (m, 3H), 6.25 (dt, *J* = 16.2 Hz, 11.3, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H).

¹³**C NMR** (125 MHz, CDCl₃) δ = 163.89 (t, *J* = 34 Hz), 162.50 (d, *J* = 248.5 Hz), 135.63 (t, *J* = 9.5 Hz), 130.31, 129.27 (d, *J* = 8.4 Hz), 118.59 (td, *J* = 25 Hz), 116.04 (d, *J* = 21.5 Hz), 112.63 (t, *J* = 247.5 Hz), 63.20, 13.97.

¹⁹**F** NMR (376 MHz, CDCl₃) δ = -103.19 (s, 2F), -110.90 (s, 1F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{12}H_{12}F_3O_2$: 245.0783, found: 245.0781.



¹**H NMR** (400 MHz, CDCl₃) δ = 7.39 – 7.34 (m, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.21 – 7.14 (m, 1H), 7.12 – 7.03 (m, 2H), 6.33 (dt, *J* = 16.2, 11.3 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ = 163.72 (t, *J* = 35 Hz), 163.02 (d, *J* = 245 Hz), 136.34 (d, *J* = 8.0 Hz), 135.67 (td, *J* = 9.4, 6.8 Hz), 130.43 (d, *J* = 8.3 Hz), 123.46, 120.27 (t, *J* = 25 Hz), 116.55 (d, *J* = 10.5 Hz), 113.88 (d, *J* = 11 Hz), 112.46 (t, *J* = 247 Hz), 63.26, 13.95.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -103.55 (s, 2F), -112.61 (s, 1F).

HRMS (ESI) (m/z): $[M+Na]^+$ calcd. for $C_{12}H_{11}F_3O_2Na$: 267.0603, found: 267.0604.



¹**H NMR** (400 MHz, CDCl₃) δ = 7.51 – 7.45 (m, 1H), 7.16 (dt, *J* = 16.4, 2.6 Hz, 1H), 6.99 – 6.77 (m, 2H), 6.39 (dt, *J* = 16.4, 11.2 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ = 163.72 (t, *J* = 35 Hz), 163.52 (dd, *J* = 251, 12.2 Hz), 161.15 (dd, *J* = 254, 12.1 Hz), 129.69 (dd, *J* = 9.9, 4.7 Hz), 128.81 (t, *J* = 9.5 Hz), 121.08 (tdd, *J* = 27.2, 22.9, 4.2 Hz), 118.55 (dd, *J* = 15.8, 3.5 Hz), 112.46 (t, *J* = 247.5 Hz), 111.96 (dd, *J* = 21.7, 3.7 Hz), 104.54 (t, *J* = 25 Hz), 63.22, 13.93.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -103.73 (s, 2F), -107.10 (d, *J* = 8.9, 1F), -111.21 (d, *J* = 8.9, 1F). **HRMS** (ESI) (m/z): [M+Na]⁺ calcd. for C₁₂H₁₀F₄O₂Na: 285.0509, found: 285.0504.



¹**H NMR** (400 MHz, CDCl₃) δ = 7.60 – 7.56 (m, 1H), 7.52 (dt, *J* = 16.2, 2.7 Hz, 1H), 7.45 – 7.39 (m, 1H), 7.33 – 7.28 (m, 2H), 6.34 (dt, *J* = 16.2, 11.1 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ = 163.70 (t, *J* = 34.5 Hz), 134.32, 133.20 (t, *J* = 9.8 Hz), 132.45, 130.56, 130.06, 127.39, 127.09, 121.61 (t, *J* = 25 Hz), 112.49 (t, *J* = 247.5 Hz), 63.21, 13.96.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -103.15 (s, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{12}H_{12}ClF_2O_2$: 261.0488, found: 261.0484.



¹**H NMR** (400 MHz, CDCl₃) δ = 7.46 (s, 1H), 7.37 – 7.31 (m, 3H), 7.04 (dt, *J* = 16.2, 2.5 Hz, 1H), 6.34 (dt, *J* = 16.2, 11.3 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ = 163.69 (t, *J* = 35 Hz), 135.93, 135.47 (t, *J* = 9.5 Hz), 134.88, 130.11, 129.59, 127.29, 125.73, 120.39 (t, *J* = 25 Hz), 112.43 (t, *J* = 247.5 Hz), 63.26, 13.96.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -103.53 (s, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{12}H_{12}CIF_2O_2$: 261.0488, found: 261.0483.



¹**H NMR** (400 MHz, CDCl₃) δ = 7.43 – 7.34 (m, 4H), 7.06 (dt, *J* = 16.2, 2.5 Hz, 1H), 6.30 (dt, *J* = 16.2, 11.3 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ = 163.78 (t, *J* = 34 Hz), 135.67, 135.56 (t, *J* = 10 Hz), 132.61,

129.10, 128.67, 119.48 (t, *J* = 25 Hz), 112.55 (t, *J* = 247.5 Hz), 63.21, 13.95.

¹⁹**F** NMR (376 MHz, CDCl₃) δ = -103.31 (dd, *J* = 11.4, 2.5 Hz, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{12}H_{12}ClF_2O_2$: 261.0488, found: 261.0484.



¹**H NMR** (400 MHz, CDCl₃) δ = 7.62 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.56 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.48 (dt, *J* = 16.1, 2.6 Hz, 1H), 7.37 - 7.33 (m, 1H), 7.23 (td, *J* = 7.8, 1.5 Hz, 1H), 6.30 (dt, *J* = 16.1, 11.1 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ = 163.68 (t, *J* = 35 Hz), 135.80 (t, *J* = 9.7 Hz), 134.21, 133.31, 130.78, 127.75, 127.55, 124.65, 121.73 (t, *J* = 25 Hz), 112.44 (t, *J* = 247.5 Hz), 63.26, 14.00.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -103.10 (s, 2F).

HRMS (ESI) (m/z): $[M+Na]^+$ calcd. for $C_{12}H_{11}BrF_2O_2Na$: 328.9782, found: 328.9778.



¹**H NMR** (400 MHz, CDCl₃) δ = 7.62 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.03 (dt, *J* = 16.2, 2.5 Hz, 1H), 6.33 (dt, *J* = 16.2, 11.3 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ = 163.69 (t, *J* = 34.6 Hz), 136.20, 135.37 (t, *J* = 9.5 Hz), 132.51,

130.37, 130.22, 126.17, 122.99, 120.43 (t, *J* = 25.1 Hz), 112.40 (t, *J* = 248.9 Hz), 63.26, 13.97.

¹⁹**F** NMR (376 MHz, CDCl₃) δ = -103.55 (dd, *J* = 11.3, 2.5 Hz, 2F).

HRMS (ESI) (m/z): $[M+Na]^+$ calcd. for $C_{12}H_{11}BrF_2O_2Na$: 326.9803, found: 326.9807.



¹**H NMR** (500 MHz, CDCl₃) δ = 7.70 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.12 (dt, *J* = 16.2, 2.3 Hz, 1H), 6.44 (dt, *J* = 16.2, 11.2 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). ¹³**C NMR** (125 MHz, CDCl₃) δ = 163.46 (t, *J* = 34.4 Hz), 138.39, 134.98 (t, *J* = 9.4 Hz), 132.67, 127.97, 122.55 (t, *J* = 25.1 Hz), 118.37, 113.02, 112.15 (t, *J* = 248.5 Hz), 63.43, 13.97. ¹⁹**F NMR** (376 MHz, CDCl₃) δ = -103.87 (s, 2F).

HRMS (ESI) (m/z): $[M+Na]^+$ calcd. for $C_{13}H_{12}NF_2O_2Na$: 274.0650, found: 274.0656.



¹**H NMR** (500 MHz, CDCl₃) δ = 8.27 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 16.2 Hz, 1H), 6.49 (dt, *J* = 16.2, 11.2 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ = 163.41 (t, *J* = 34.2 Hz), 148.26, 140.22, 134.55 (t, *J* = 9.3 Hz), 128.20, 124.19, 123.27 (t, *J* = 25.2 Hz), 112.07 (t, *J* = 249.5 Hz), 63.48, 13.98. ¹⁹**F NMR** (376 MHz, CDCl₃) δ = -103.95 (s, 2F).

HRMS (ESI) (m/z): $[M+Na]^+$ calcd. for $C_{12}H_{11}NF_2O_4Na$: 294.0548, found: 294.0545.



¹**H NMR** (400 MHz, CDCl₃) δ = 8.11 (d, *J* = 8.2 Hz, 1H), 7.97 – 7.87 (m, 3H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.63 – 7.48 (m, 3H), 6.42 (dt, *J* = 15.9, 11.4 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). ¹³**C NMR** (125 MHz, CDCl₃) δ = 163.98 (t, *J* = 34.8 Hz), 134.35 (t, *J* = 9.5 Hz), 133.61, 131.76, 131.15, 129.92, 128.74, 126.79, 126.24, 125.49, 124.74, 123.33, 121.86 (t, *J* = 24.8 Hz), 112.66 (t, *J* = 248.7 Hz), 63.23, 14.03.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -102.99 (s, 2F).

HRMS (ESI) (m/z): $[M+Na]^+$ calcd. for $C_{16}H_{14}F_2O_2Na$: 299.0854, found: 299.0851.



¹**H** NMR (400 MHz, CDCl₃) δ = 7.41 – 7.39 (m, 3H), 7.37 – 7.32 (m, 3H), 7.31 – 7.27 (m, 2H), 7.27 – 7.20 (m, 2H), 6.30 (t, *J* = 11.8 Hz, 1H), 3.93 (q, *J* = 7.2 Hz, 2H), 1.20 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ = 163.49 (t, J = 34 Hz), 151.01 (t, J = 9.0 Hz), 140.50, 137.10, 129.86, 129.11, 128.59, 128.41, 128.01, 127.91, 119.50 (t, J = 28 Hz), 112.56 (t, J = 245 Hz), 62.77, 13.69.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -90.96 (d, *J* = 11.9 Hz, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{18}H_{17}F_2O_2$: 303.1191, found: 303.1186.



¹**H NMR** (400 MHz, CDCl₃) δ = 8.14 (d, *J* = 7.8 Hz, 1H), 7.66 (t, *J* = 7.4 Hz, 3H), 7.46 – 7.39 (m, 2H), 7.35 – 7.29 (m, 2H), 6.67 (t, *J* = 15.8 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ = 163.57 (t, J = 34.8 Hz), 143.87 (t, J = 7.6 Hz), 142.29, 140.18, 138.10, 134.00, 130.44, 130.19, 127.77, 127.51, 127.20 (t, J = 7.4 Hz), 121.03, 119.78, 119.75, 115.19 (t, J = 29.4 Hz), 112.91 (t, J = 248.0 Hz), 63.46, 13.93.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -96.01 (s, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{18}H_{15}F_2O_2$: 301.1035, found: 301.1032.



¹**H NMR** (500 MHz, CDCl₃) δ = 7.38 (t, *J* = 7.6 Hz, 2H), 7.35 – 7.27 (m, 3H), 6.95 (s, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.99 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ = 164.05 (t, J = 35.2 Hz), 135.23, 131.01 (t, J = 9.2 Hz), 129.21,

128.39, 127.96, 114.42 (t, *J* = 251.3 Hz), 63.03, 14.00, 12.56 (t, *J* = 2.8 Hz).

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -106.62 (s, 2F).

HRMS (ESI) (m/z): $[M+Na]^+$ calcd. for $C_{13}H_{14}F_2O_2Na$: 263.0854, found: 263.0854.



¹**H NMR** (400 MHz, CDCl₃) δ = 4.37 (q, J = 7.1 Hz, 2H), 1.64 – 1.54 (m, 5H), 1.39 (t, J = 7.1 Hz,

4H), 1.21 (dd, *J* = 7.3, 5.0 Hz, 12H).

¹³C NMR (100 MHz, CDCl₃) δ = 160.74 (t, J = 42.7 Hz), 115.54 (t, J = 267.6 Hz), 62.99, 61.39, 40.21, 33.41 (t, J = 4.3 Hz), 20.76, 16.92, 13.92.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -73.45 (s, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{13}H_{24}NF_2O_3$: 280.1719, found: 280.1714.



¹**H NMR** (400 MHz, CDCl₃) δ = 7.38 – 7.29 (m, 5H), 6.75 (t, *J* = 10.9 Hz, 1H), 3.99 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (*E*) (101 MHz, CDCl₃) δ = 162.54 (t, *J* = 34 Hz), 140.69, 133.05 (t, *J* = 28.5 Hz),

129.46, 128.51, 128.07, 127.84 (t, *J* = 1.5 Hz), 110.87 (t, *J* = 250 Hz), 63.14, 13.71.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -93.79 (*E*, 2F), -98.07 (*Z*, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{12}H_{12}F_2O_2I$: 352.9845, found: 352.9842.



¹**H NMR** (*E*) (500 MHz, CDCl₃) δ = 7.22 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.71 (t, *J* = 10.9 Hz, 1H), 4.00 (q, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H). ¹³**C NMR** (*E*) (126 MHz, CDCl₃) δ = 162.61 (t, *J* = 34 Hz), 139.69, 137.88, 132.72 (t, *J* = 28.5 Hz), 129.15, 128.72, 127.86, 110.91 (t, *J* = 250.7 Hz), 63.12, 21.37, 13.70. ¹⁹**F NMR** (376 MHz, CDCl₃) δ = -93.27 (*E*, 2F), -97.56 (*Z*, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{13}H_{14}F_2O_2I$: 367.0001, found: 366.9998.



¹**H** NMR (*E*) (400 MHz, CDCl₃) δ = 7.31 – 7.26 (m, 2H), 6.86 – 6.82 (m, 2H), 6.69 (t, *J* = 10.8 Hz, 1H), 4.01 (q, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H).

¹**H NMR** (*Z*) (400 MHz, CDCl₃) δ = 7.48 (d, *J* = 8.9, 2H), 6.88 (d, *J* = 8.9, 2H), 6.62 (d, *J* = 11.9,

1H), 4.42 (q, *J* = 7.1, 2H), 3.86 (s, 3H), 1.41 (t, *J* = 7.1, 3H).

¹³**C NMR** (*E*) (126 MHz, CDCl₃) δ = 162.63 (t, *J* = 33.4 Hz), 160.32, 132.99, 132.52 (t, *J* = 28.5 Hz), 129.72, 128.39 (t, *J* = 30 Hz), 113.37, 110.93 (t, *J* = 251 Hz), 63.14, 55.36, 13.73.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -93.68 (*E*, 2F), -97.83 (*Z*, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{13}H_{14}F_2O_3I$: 382.9950, found: 382.9946.



¹**H NMR** (*E*) (500 MHz, CDCl₃) δ = 7.34 – 7.31 (m, 2H), 7.28 – 7.25 (m, 2H), 6.74 (t, *J* = 11.3 Hz, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H).

¹**H NMR** (*Z*) (500 MHz, CDCl₃) δ = 7.46 (d, *J* = 8.6, 2H), 7.36 (d, *J* = 8.7, 2H), 6.69 (d, *J* = 11.6, 1H), 4.43 (q, *J* = 7.1, 2H), 1.42 (t, *J* = 7.1, 3H).

¹³**C NMR** (*E*) (126 MHz, CDCl₃) δ = 162.54 (t, *J* = 33.4 Hz), 139.23, 135.41, 133.44 (t, *J* = 28 Hz), 129.15, 128.33, 110.86 (t, *J* = 252 Hz), 106.99 (t, *J* = 9.4 Hz), 63.37, 13.76.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -94.63 (*E*, 2F), -98.25 (*Z*, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{12}H_{11}ClF_2O_2I$: 386.9455, found: 386.9448.



¹**H NMR** (*E*) (500 MHz, CDCl₃) δ = 7.48 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 6.74 (t, *J* = 11.3 Hz, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H).

¹**H NMR** (*Z*) (500 MHz, CDCl₃) δ = 7.51 (d, *J* = 8.6, 2H), 7.39 (d, *J* = 8.6, 2H), 6.69 (d, *J* = 11.6,

1H), 4.42 (q, *J* = 7.1, 2H), 1.42 (t, *J* = 7.1, 3H).

¹³**C NMR** (*E*) (126 MHz, CDCl₃) δ = 162.54(t, *J* = 33.4 Hz), 139.71, 133.41 (t, *J* = 28 Hz), 131.30, 129.34, 123.68, 110.87 (t, *J* = 252 Hz), 106.96, 63.39, 13.77.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -94.67 (*E*, 2*F*), -98.29 (*Z*, 2*F*).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{12}H_{11}BrF_2O_2I$: 430.8950, found: 430.8945.



¹**H** NMR (*E*) (500 MHz, CDCl₃) δ = 7.35 – 7.31 (m, 1H), 7.17 (dd, *J*= 7.6, 1.6 Hz, 1H), 6.94 (td, *J* = 7.5, 0.9 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 6.76 (t, *J* = 11.0 Hz, 1H), 4.05 (q, *J* = 7.2 Hz, 2H), 3.88 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (*E*) (126 MHz, CDCl₃) δ = 162.57 (t, *J* = 33.4 Hz), 155.22, 133.95 (t, *J* = 28 Hz), 130.98, 129.16, 129.05, 120.08, 111.02, 110.94 (t, *J* = 252 Hz), 103.72 (t, *J* = 10 Hz), 62.98, 55.58, 13.75.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -97.05 (*E*, 2F), -98.59 (*Z*, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{13}H_{14}F_2O_3I$: 382.9950, found: 382.9943.



¹**H NMR** (*E*) (500 MHz, CDCl₃) δ = 7.25 (t, *J* = 7.9 Hz, 1H), 6.93 – 6.90 (m, 1H), 6.88 – 6.86 (m, 1H), 6.85 – 6.81 (m, 1H), 6.72 (t, *J* = 10.9 Hz, 1H), 4.01 (q, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H).

¹³**C NMR** (*E*) (126 MHz, CDCl₃) δ = 162.54 (t, *J* = 33.4 Hz), 158.83, 141.73, 133.03 (t, *J* = 28 Hz), 129.18, 120.30, 115.45, 113.11, 110.87 (t, *J* = 252 Hz), 108.40 (t, *J* = 10.4 Hz), 63.17, 55.33, 13.69.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -93.74 (*E*, 2F), -98.09 (*Z*, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{13}H_{14}F_2O_3I$: 382.9950, found: 382.9945.



¹**H NMR** (*E*) (500 MHz, CDCl₃) δ = 7.57 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 6.74 (t, *J* = 11.5 Hz, 1H), 4.07 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (*E*) (126 MHz, CDCl₃) δ = 162.50 (t, *J* = 33.4 Hz), 144.33, 133.78 (t, *J* = 28 Hz), 131.04, 128.05, 125.10 (q, *J* = 3.7 Hz), 122.55, 110.87 (t, *J* = 252 Hz), 106.01 (t, *J* = 8.9 Hz), 63.44, 13.73.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -62.82 (*Z*, 3F), -62.92 (*E*, 3F), -95.28 (*E*, 2F), -98.65 (*Z*, 2F). **HRMS** (ESI) (m/z): [M+H]⁺ calcd. for C₁₃H₁₁F₅O₂I: 420.9718, found: 420.9716.



¹**H NMR** (*E*) (500 MHz, CDCl₃) δ = 7.48 – 7.44 (m, 2H), 7.27 – 7.19 (m, 2H), 6.74 (t, *J* = 11.2 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (*E*) (126 MHz, CDCl₃) δ = 162.46 (t, *J* = 33.4 Hz), 142.54, 133.81 (t, *J* = 28 Hz), 132.39, 130.47, 129.63, 126.38, 121.82, 110.81 (t, *J* = 252 Hz), 105.86 (t, *J* = 9.5 Hz), 63.43, 13.78.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -94.78(*E*, 2F), -98.44 (*Z*, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{12}H_{14}BrF_2O_2I$: 430.8950, found: 430.8947.



¹**H NMR** (*E*) (400 MHz, CDCl₃) δ = 7.65 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 6.77 (t, *J* = 11.9 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H).

¹³**C** NMR (*E*) (101 MHz, CDCl₃) δ = 162.39 (t, *J* = 33.4 Hz), 145.34, 133.86 (t, *J* = 28 Hz), 131.86, 128.30, 118.06, 113.00, 110.88 (t, *J* = 252 Hz), 105.12, 63.56, 13.82.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -95.94 (*E*, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{13}H_{11}NF_2O_2I$: 377.9797, found: 377.9792.



¹**H NMR** (*E*) (400 MHz, CDCl₃) δ = 10.27 (s, 1H), 7.91 (dd, *J* = 7.7 Hz, 1.3, 1H), 7.60 (td, *J* = 7.6, 1.4 Hz, 1H), 7.51 (td, *J* = 7.6, 0.7 Hz, 1H), 7.28 (t, *J* = 3.4 Hz, 1H), 6.88 (t, *J* = 11.5 Hz, 1H), 4.21 – 4.10 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (*E*) (101 MHz, CDCl₃) δ = 190.14, 162.34 (t, *J* = 33.4 Hz), 142.90, 134.70 (t, *J* = 28 Hz), 133.57, 131.07, 129.77, 129.39, 128.39, 110.97 (t, *J* = 252 Hz), 102.94 (t, *J* = 10 Hz), 63.47,

13.75.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -97.27 (*E*, 1F), -97.46 (*E*, 1F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{13}H_{12}F_2O_3I$: 380.9794, found: 380.9789.



¹**H NMR** (*E*) (400 MHz, CDCl₃) δ = 7.37 – 7.29 (m, 2H), 7.06 – 7.00 (m, 2H), 6.74 (t, *J* = 11.2 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (*E*) (101 MHz, CDCl₃) δ = 162.90 (d, *J* = 252 Hz), 162.53 (t, *J* = 33.4 Hz), 136.87, 133.41(t, *J* = 28 Hz), 129.93 (d, *J* = 8.5 Hz), 115.29 (d, *J* = 23 Hz), 110.85 (t, *J* = 252 Hz), 107.32 (t, *J* = 9.7 Hz), 63.27, 13.74.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -94.34 (*E*, 2F), -98.16 (*Z*, 2F), -110.59 (*E*, F), -110.84 (*Z*, F). **HRMS** (ESI) (m/z): [M+H]⁺ calcd. for C₁₂H₁₁F₃O₂I: 370.9750, found: 370.9745.



¹**H NMR** (*E*) (400 MHz, CDCl₃) δ = 8.22 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 6.80 (t, *J* = 12.0 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.36 – 1.26 (m, 3H).

¹³C NMR (*E*) (101 MHz, CDCl₃) δ = 162.37 (t, *J* = 33.4 Hz), 147.19, 134.04 (t, *J* = 28 Hz), 132.98, 128.56, 123.33, 110.92 (t, *J* = 252 Hz), 104.50 (t, *J* = 8.3 Hz), 63.61, 13.83.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -96.27 (*E*, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{12}H_{11}F_2NO_4I$: 397.9695, found: 397.9691.



¹**H NMR** (*E*) (400 MHz, CDCl₃) δ = 7.24 (d, *J* = 7.3 Hz, 1H), 7.18 (t, *J* = 7.0 Hz, 2H), 7.12 (d, *J* = 7.5 Hz, 1H), 6.78 (t, *J* = 10.6 Hz, 1H), 4.01 (q, *J* = 7.1 Hz, 2H), 2.30 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (E) (101 MHz, CDCl₃) δ = 162.52 (t, J = 33.4 Hz), 139.69, 134.82, 133.74 (t, J = 28 Hz), 130.34, 129.42, 127.23, 125.52, 110.77 (t, J = 250 Hz), 107.93 (t, J = 9.9 Hz), 63.13, 19.45,

13.70.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -95.39, -96.12, -97.44, -98.16.

HRMS (ESI) (m/z): $[M+Na]^+$ calcd. for $C_{13}H_{13}F_2O_2INa$: 388.9821, found: 388.9815.



¹**H** NMR (*E*) (400 MHz, CDCl₃) δ = 7.41 – 7.36 (m, 1H), 7.31 – 7.27 (m, 2H), 7.26 – 7.23 (m, 1H), 6.81 (t, *J* = 11.4 Hz, 1H), 4.21 – 4.13 (m, 2H), 1.30 (t, *J* = 7.2 Hz, 3H).

¹³**C NMR** (*E*) (101 MHz, CDCl₃) δ = 162.31 (t, *J* = 33.4 Hz), 138.89, 134.66 (t, *J* = 28 Hz), 131.44, 130.46, 129.81, 128.92, 126.58, 110.87 (t, *J* = 252 Hz), 103.38 (t, *J* = 9.0 Hz), 63.34, 13.80.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -97.96 (*E*, 2F), -99.39 (*Z*, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{12}H_{11}F_2O_2IC1$: 386.9455, found: 386.9456.



¹**H NMR** (*E*) (400 MHz, CDCl₃) δ = 8.02 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 6.76 (t, *J* = 11.4 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 4.09 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (E) (101 MHz, CDCl₃) δ = 165.71, 162.47 (t, J = 33.4 Hz), 145.00, 133.46 (t, J = 28 Hz), 131.10, 129.27, 127.66, 110.87 (t, J = 252 Hz), 106.80 (t, J = 9.4 Hz), 63.36, 61.26, 14.30, 13.76.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -95.11 (*E*, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{15}H_{16}F_2O_4I$: 425.0056, found: 425.0040.



¹**H NMR** (*E*) (500 MHz, CDCl₃) δ = 7.58 (d, *J* = 8.1 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 6.78 (t, *J* = 11.4 Hz, 1H), 4.19 (dd, *J* = 13.5, 6.6 Hz, 2H), 1.31 (t, *J* = 6.9 Hz, 3H).

¹³C NMR (*E*) (126 MHz, CDCl₃) δ = 162.31 (t, *J* = 33.4 Hz), 140.75, 134.28 (t, *J* = 28 Hz), 133.01, 130.49, 128.89, 127.18, 121.08, 110.89 (t, *J* = 252 Hz), 105.57 (t, *J* = 8.8 Hz), 63.37, 13.84.

¹⁹**F** NMR (376 MHz, CDCl₃) δ = -98.02 (*E*, 1F), -98.19 (*E*, 1F), -98.90 (*Z*, 1F), -99.49 (*Z*, 1F). **HRMS** (ESI) (m/z): [M+H]⁺ calcd. for C₁₂H₁₁F₂O₂IBr: 430.8950, 432,8929, found: 430.8942, 432,8921.

CF2CO2CH3

¹**H NMR** (*Z*) (400 MHz, CDCl₃) δ = 7.40 – 7.33 (m, 5H), 6.99 (d, *J* = 12.5 Hz, 1H), 5.90 (q, *J* = 12.9 Hz, 1H), 3.61 (s, 3H).

¹³**C NMR** (*Z*) (126 MHz, CDCl₃) δ = 163.91 (t, *J* = 34 Hz), 138.92 (t, *J* = 8.8 Hz), 134.18, 128.86 (t, *J* = 3.3 Hz), 128.23, 127.48, 121.88 (t, *J* = 27.7 Hz), 112.25 (t, *J* = 247 Hz), 53.28.

¹⁹**F** NMR (376 MHz, CDCl₃) δ = -94.16 (*Z*, 2F), -103.11 (*E*, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{11}H_{11}F_2O_2$: 213.0722, found: 213.0720.

CF2CO2C2H5

¹**H NMR** (*Z*) (500 MHz, CDCl₃) δ = 7.39 – 7.34 (m, 5H), 6.98 (d, *J* = 12.6 Hz, 1H), 5.90 (q, *J* = 12.9 Hz, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 1.15 (t, *J* = 7.2 Hz, 3H).

¹³**C NMR** (*Z*) (126 MHz, CDCl₃) δ = 163.42 (t, *J* = 34 Hz), 138.76 (t, *J* = 8.9 Hz), 134.27, 128.93

(t, J = 2.7 Hz), 128.75, 128.23, 121.96 (t, J = 27.7 Hz), 112.28 (t, J = 247 Hz), 62.95, 13.62.

¹⁹**F** NMR (376 MHz, CDCl₃) δ = -93.94 (*Z*, 2F), -103.24 (*E*, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{12}H_{13}F_2O_2$: 227.0878, found: 227.0876.



¹**H NMR** (*Z*) (500 MHz, CDCl₃) δ = 7.44 – 7.34 (m, 2H), 7.33 – 7.25 (m, 2H), 7.06 (d, *J* = 12.3 Hz, 1H), 6.03 (q, *J* = 12.3 Hz, 1H), 3.63 (s, 3H).

¹³C NMR (*Z*) (126 MHz, CDCl₃) δ = 163.61 (t, *J* = 34 Hz), 136.10 (t, *J* = 8.9 Hz), 133.10, 132.96, 130.95 (t, *J* = 3.3 Hz), 130.02, 129.02, 126.48, 123.62 (t, *J* = 27.7 Hz), 112.04 (t, *J* = 247 Hz),

53.30.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -95.08 (Z, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{11}H_{10}ClF_2O_2$: 247.0332, found: 247.0329.



¹H NMR (*Z*) (500 MHz, CDCl₃) δ = 7.42 – 7.37 (m, 2H), 7.33 – 7.24 (m, 2H), 7.06 (d, *J* = 12.3 Hz, 1H), 6.03 (q, *J* = 12.3 Hz, 1H), 4.04 (q, *J* = 7.2 Hz, 2H), 1.20 (t, *J* = 7.2 Hz, 3H).

¹³**C NMR** (*Z*) (126 MHz, CDCl₃) δ = 163.13 (t, *J* = 34 Hz), 135.87 (t, *J* = 8.8 Hz), 133.19, 132.99, 130.99 (t, *J* = 3.5 Hz), 130.03, 129.02, 126.49, 123.68 (t, *J* = 27.7 Hz), 112.07 (t, *J* = 247 Hz), 63.05, 13.61.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -94.72 (*Z*, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{12}H_{12}ClF_2O_2$: 261.0488, found: 261.0484.



¹**H** NMR (*Z*) (500 MHz, CDCl₃) δ = 7.29 – 7.24 (m, 2H), 7.21 – 7.17 (m, 2H), 6.94 (d, *J* = 12.6 Hz, 1H), 5.84 (q, *J* = 13.1 Hz, 1H), 3.64 (s, 3H), 2.37 (s, 3H).

¹³**C NMR** (*Z*) (126 MHz, CDCl₃) δ = 164.02 (t, *J* = 34 Hz), 138.94 (t, *J* = 8.8 Hz), 131.30, 129.58, 128.94, 127.42, 120.94 (t, *J* = 27.7 Hz), 112.37 (t, *J* = 247 Hz), 53.29, 21.31.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -94.19 (Z, 2F), -102.85 (E, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{12}H_{13}F_2O_2$: 227.0878, found: 227.0874.



¹**H** NMR (*Z*) (500 MHz, CDCl₃) δ = 7.28 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 12.6 Hz, 1H), 5.84 (q, *J* = 13.2 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (*Z*) (126 MHz, CDCl₃) δ = 163.53 (t, *J* = 34 Hz), 138.78 (t, *J* = 8.8 Hz), 131.39, 129.57, 128.93, 127.42, 121.04 (t, *J* = 27.7 Hz), 112.40 (t, *J* = 247 Hz), 62.92, 21.30, 13.63.
¹⁹**F NMR** (376 MHz, CDCl₃) δ = -94.01 (Z, 2F), -102.99 (E, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{13}H_{15}F_2O_2$: 241.1035, found: 241.1030.



¹**H NMR** (*Z*) (400 MHz, CDCl₃) δ = 7.42 – 7.29 (m, 4H), 6.91 (d, *J* = 12.6 Hz, 1H), 5.90 (q, *J* = 13.2 Hz, 1H), 3.70 (s, 3H). ¹³**C NMR** (*Z*) (126 MHz, CDCl₃) δ = 163.88 (t, *J* = 34 Hz), 137.66 (t, *J* = 8.3 Hz), 134.79, 132.55, 130.31 (t, *J* = 3.0 Hz), 128.45, 122.21 (t, *J* = 27.7 Hz), 112.13 (t, *J* = 247 Hz), 53.47. ¹⁹**F NMR** (376 MHz, CDCl₃) δ = -95.17 (*Z*, 2F), -103.22 (*E*, 2F). **HRMS** (ESI) (m/z): [M+H]⁺ calcd. for C₁₁H₁₀ClF₂O₂: 247.0332, found: 247.0328.

CI CF₂CO₂C₂H₅

¹**H NMR** (*Z*) (400 MHz, CDCl₃) δ = 7.38 – 7.30 (m, 4H), 6.90 (dt, *J* = 12.6, 1.7 Hz, 1H), 5.90 (q, *J* = 13.2 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H).

¹³**C NMR** (*Z*) (126 MHz, CDCl₃) δ = 163.38 (t, *J* = 34 Hz), 137.49 (t, *J* = 8.4 Hz), 134.78, 132.64,

130.37, 128.44, 122.35 (t, *J* = 27.7 Hz), 112.16 (t, *J* = 247 Hz), 63.13, 13.71.

¹⁹**F** NMR (376 MHz, CDCl₃) δ = -95.03 (*Z*, 2F), -103.36 (*E*, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{12}H_{12}CIF_2O_2$: 261.0488, found: 261.0486.

Br CF₂CO₂CH₃

¹**H** NMR (*Z*) (400 MHz, CDCl₃) δ = 7.50 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 12.6 Hz, 1H), 5.91 (q, *J* = 13.1 Hz, 1H), 3.70 (s, 3H).

¹³**C NMR** (*Z*) (126 MHz, CDCl₃) δ = 163.86 (t, *J* = 34 Hz), 137.69 (t, *J* = 8.2 Hz), 133.01, 131.41,

130.54 (t, *J* = 3.0 Hz), 123.05, 122.28 (t, *J* = 27.7 Hz), 112.13 (t, *J* = 247 Hz), 53.49.

¹⁹**F** NMR (376 MHz, CDCl₃) δ = -95.22 (Z, 2F), -103.26 (E, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{11}H_{10}BrF_2O_2$: 290.9827, 292.9806, found: 290.9823, 292.9801.

¹**H NMR** (*Z*) (400 MHz, CDCl₃) δ = 7.50 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 12.6 Hz, 1H), 5.91 (1, *J* = 13.2 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H). ¹³**C NMR** (*Z*) (126 MHz, CDCl₃) δ = 163.37 (t, *J* = 34 Hz), 137.53 (t, *J* = 8.3 Hz), 133.10, 131.41, 130.60 (t, *J* = 3.0 Hz), 123.04, 122.43 (t, *J* = 27.7 Hz), 112.15 (t, *J* = 247 Hz), 63.15, 13.71. ¹⁹**F NMR** (376 MHz, CDCl₃) δ = -95.08 (*Z*, 2F), -103.40 (*E*, 2F). **HRMS** (ESI) (m/z): [M+H]⁺ calcd. for C₁₂H₁₂BrF₂O₂: 304.9983, 306.9963, found: 304.9977, 306.9957.



¹**H** NMR (*Z*) (400 MHz, CDCl₃) δ = 7.29 – 7.24 (m, 2H), 7.15 (d, *J* = 6.9 Hz, 2H), 6.96 (d, *J* = 12.5 Hz, 1H), 5.88 (q, *J* = 12.8 Hz, 1H), 3.59 (s, 3H), 2.37 (s, 3H).

¹³C NMR (Z) (126 MHz, CDCl₃) δ = 163.91 (t, J = 34 Hz), 139.03 (t, J = 9.0 Hz), 137.88, 134.12, 129.52 (t, J = 2.5 Hz), 129.47, 128.15, 125.86 (t, J = 2.8 Hz), 121.70 (t, J = 27.7 Hz), 112.27 (t, J = 247 Hz), 53.21, 21.33.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -93.78 (*Z*, 2F), -103.06 (*E*, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{12}H_{13}F_2O_2$: 227.0878, found: 227.0875.



¹**H NMR** (*Z*) (400 MHz, CDCl₃) δ = 7.28 – 7.24 (m, 2H), 7.17 – 7.14 (m, 2H), 6.95 (d, *J* = 12.6 Hz, 1H), 5.88 (q, *J* = 12.8 Hz, 1H), 4.04 (q, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H). ¹³**C NMR** (*Z*) (126 MHz, CDCl₃) δ = 163.41 (t, *J* = 34 Hz), 138.87 (t, *J* = 9.1 Hz), 137.88, 134.22, 129.57 (t, *J* = 2.5 Hz), 129.48, 128.16, 125.96 (t, *J* = 2.8 Hz), 121.78 (t, *J* = 27.7 Hz), 112.31 (t, *J* = 247 Hz), 62.89, 21.33, 13.58.

¹⁹**F** NMR (376 MHz, CDCl₃) δ = -93.59 (Z, 2F), -103.18 (E, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{13}H_{15}F_2O_2$: 241.0878, found: 241.0872.



¹**H NMR** (*Z*) (400 MHz, CDCl₃) δ = 7.35 – 7.31 (m, 1H), 7.30 – 7.28 (m, 1H), 7.07 (d, *J* = 12.4 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 5.92 (q, *J* = 12.5 Hz, 1H), 3.85 (s, 3H), 3.59 (s, 3H).

¹³C NMR (*Z*) (126 MHz, CDCl₃) δ = 163.96 (t, *J* = 34 Hz), 156.81, 134.86 (t, *J* = 8.9 Hz), 130.47 (t, *J* = 2.5 Hz), 130.33, 123.41, 121.96 (t, *J* = 27.7 Hz), 120.17, 112.47 (t, *J* = 247 Hz), 110.07, 55.46, 53.13.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -94.73 (Z, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{12}H_{13}F_2O_3$: 243.0827, found: 243.0824.



¹**H NMR** (*Z*) (400 MHz, CDCl₃) δ = 7.35 – 7.31 (m, 2H), 7.07 (d, *J* = 12.4 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 5.92 (q, *J* = 12.5 Hz, 1H), 4.01 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (Z) (126 MHz, CDCl₃) δ = 163.19 (t, J = 34 Hz), 156.86, 134.69 (t, J = 9.1 Hz), 130.53 (t, J = 2.5 Hz), 130.36, 123.50, 121.96 (t, J = 27.7 Hz), 120.17, 112.50 (t, J = 247 Hz), 110.02, 62.78, 55.41, 13.57.

¹⁹**F** NMR (376 MHz, CDCl₃) δ = -94.29 (Z, 2F), -102.92 (E, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{13}H_{15}F_2O_3$: 257.0984, found: 257.0980.



¹**H** NMR (*Z*) (500 MHz, CDCl₃) δ = 7.60 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.25 – 7.19 (m, 1H), 7.00 (d, *J* = 12.3 Hz, 1H), 6.01 (q, *J* = 12.1 Hz, 1H), 3.62 (s, 3H).

¹³C NMR (Z) (126 MHz, CDCl₃) δ = 163.56 (t, J = 34 Hz), 138.05 (t, J = 8.9 Hz), 134.83, 132.16, 131.04 (t, J = 3.2 Hz), 130.15, 127.09, 123.36 (t, J = 27.7 Hz), 122.92, 112.00 (t, J = 247 Hz), 53.31.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -94.86 (Z, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{11}H_{10}BrF_2O_2$: 290.9827, 292.9806, found: 290.9822, 292.9801.



¹**H** NMR (*Z*) (500 MHz, CDCl₃) δ = 7.59 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.32 (td, *J* = 7.5, 0.9 Hz, 1H), 7.22 (td, *J* = 7.6, 1.4 Hz, 1H), 7.00 (d, *J* = 12.2 Hz, 1H), 6.01 (q, *J* = 12.2 Hz, 1H), 4.03 (q, *J* = 7.2 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (Z) (126 MHz, CDCl₃) δ = 163.10 (t, J = 34 Hz), 137.85 (t, J = 8.9 Hz), 134.83, 132.18, 131.07 (t, J = 3.3 Hz), 130.15, 127.10, 123.40 (t, J = 22.7 Hz), 123.07, 112.03 (t, J = 247 Hz), 63.06, 13.65.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -94.52 (*Z*, 2F), -103.11 (*E*, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{12}H_{12}BrF_2O_2$: 304.9983, 306.9963, found: 304.9977, 306.9957.



¹**H** NMR (*Z*) (500 MHz, CDCl₃) δ = 7.27 – 7.23 (m, 1H), 7.19 (d, *J* = 4.8 Hz, 3H), 7.04 (d, *J* = 12.2 Hz, 1H), 5.99 (q, *J* = 11.9 Hz, 1H), 3.46 (s, 3H), 2.28 (s, 3H).

¹³**C NMR** (*Z*) (126 MHz, CDCl₃) δ = 163.69 (t, *J* = 34 Hz), 138.35 (t, *J* = 9.7 Hz), 135.98, 133.73, 129.49, 129.21 (t, *J* = 2.7 Hz), 128.78, 125.55, 123.09 (t, *J* = 22.7 Hz), 112.22 (t, *J* = 247 Hz), 53.03, 19.79.

¹⁹**F** NMR (376 MHz, CDCl₃) δ = -93.86 (*Z*, 2F), -103.03 (*E*, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{12}H_{13}F_2O_2$: 227.0878, found: 227.0874.



¹**H NMR** (*Z*) (500 MHz, CDCl₃) δ = 7.27 – 7.16 (m, 4H), 7.03 (d, *J* = 12.2 Hz, 1H), 5.99 (q, *J* = 11.7 Hz, 1H), 3.89 (q, *J* = 7.2 Hz, 2H), 2.29 (s, 3H), 1.14 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (Z) (126 MHz, CDCl₃) δ = 163.28 (t, J = 34 Hz), 138.10 (t, J = 9.5 Hz), 135.99, 133.83, 129.50, 129.20 (t, J = 2.8 Hz), 128.77, 125.55, 123.04 (t, J = 22.7 Hz), 112.26 (t, J = 247 Hz), 62.79, 19.87, 13.56.

¹⁹**F NMR** (376 MHz, CDCl₃) δ = -93.71 (*Z*, 2F), -103.09 (*E*, 2F).

HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{13}H_{15}F_2O_2$: 241.0878, found: 241.0872.

3. NMR spectra



130 90 60 30 0 -30 -70 -110 -160 -210 f1 (ppm)







































10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 f1 (ppm)









90 80 f1 (ppm)









) 80 f1 (ppm)



















170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)













170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)















200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)



4.0 3.5 f1 (ppm)

3.0

2.5

4.5

5.5

5.0

6.5

6.0

1.5

0.5

1.0

0.0

2.0

70



10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 f1 (ppm)



170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)










f1 (ppm) . 140 . 130 . 30







10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 f1 (ppm)



170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)





























160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)























10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 f1 (ppm)















90 80 f1 (ppm)





















CHO | CF₂CO₂Et
















 ~ -97.96 ~ -99.39









































- 53. 31

























90 80 f1 (ppm) 140 130 120 110









